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SOLUBILITY OF SOLIDS IN DENSE GASES

J. M. PRAUSNITZ



U. S. DEPARTMENT OF COMMERCE
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ABSTRACT

The thermodynamics of solid-dense gas equilibria is discussed, and two techniques are described for calculating the solubility of a solid component in a gas at high pressure. The first one is based on the recent empirical equation of state of Redlich which, in turn, is derived from Pitzer's generalized tables of fluid-phase volumetric properties. The second one is based on the Hildebrand-Scatchard theory of solutions. Both methods give good semiquantitative results but cannot accurately predict solubilities from pure-component data alone.

1. Introduction

High-pressure processes are becoming increasingly important in the chemical and related industries; it is therefore of practical interest to develop techniques for the prediction of phase equilibria at advanced pressures. In this report we consider the equilibrium between a solid and a dense gas, i.e., a gas at pressures around 100-300 atm. In particular, we attempt to calculate the solubility of the heavy (solid) component in the light (gaseous) component. Experimental studies have repeatedly shown that such solubilities are very much larger than those computed by a simple calculation, which assumes ideal-gas behavior. Indeed, the ratio, of observed solubility to solubility calculated on the basis of ideality, is often of the order of 10^3 ; in some cases it is as high as 10^6 [1].

We discuss two techniques for calculating the solubility of a solid in a dense gas. One is based on a new empirical equation of state recently developed by Redlich and co-workers; the other one is based on the regular solution concept of Hildebrand and Scatchard [2]. Unfortunately neither of these techniques is capable of giving very accurate quantitative predictions of the desired solubility. Both techniques however show the correct trends and give reasonable results. Furthermore, the application of regular solution theory to this problem offers a method

of correlating and extending experimental data in a rational manner.

Before describing these two techniques we review briefly the basic thermodynamics and previously presented attempts to deal with the problem of solubility of solids in compressed gases.

2. Basic Thermodynamic Equations

Let subscript 2 refer to the heavy (solid) component and let subscript 1 refer to the light (gaseous) component. The equation of equilibrium is

$$f_2^s = f_2^g, \quad (1)$$

where f stands for fugacity, superscript s stands for solid, and g stands for gas. The fugacity of the solid at temperature T and total pressure P is easily calculated from solid vapor pressure and density data. We assume that the solid is pure, i. e., the gaseous component 1 does not dissolve appreciably in the solid phase:

$$f_2^s = P_2^s \varphi_2^s \exp \int_{P_2^s}^P \frac{v_2^s dP}{RT}, \quad (2)$$

where s = saturation,

P_2^s = saturation (vapor) pressure of the solid at T ,

v_2^s = molar volume of the solid at T , and

φ_2^s = fugacity coefficient of saturated vapor at T and P_2^s .

In almost all cases of practical interest, P_2^s is small and thus $\varphi_2^s \approx 1$. Further, the solid may be considered to be incompressible and thus (2) becomes

$$f_2^s = P_2^s \exp \frac{v_2^s (P - P_2^s)}{RT} \quad (2a)$$

The fugacity of component 2 in the gas phase is related to y_2 , its mole fraction (i. e., the solubility) in that phase, by

$$f_2^g = \varphi_2 y_2 P, \quad (3)$$

where φ_2 is the fugacity coefficient of 2 in the gas mixture at temperature T , composition y_2 and total pressure P . The entire problem of calculating the desired solubility lies in the calculation of φ_2 .

The fugacity coefficient φ_2 can be found from the rigorous thermodynamic relation [3],

$$\ln \varphi_2 = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_2} \right)_{T, V, n_1} - \frac{RT}{V} \right] dV - \ln z, \quad (4)$$

where V is the volume of the gas mixture at T and P having n_1 moles of 1 and n_2 moles of 2, and where z is the compressibility factor of the

mixture:

$$z = \frac{PV}{(n_1 + n_2) RT} \quad (5)$$

In order to utilize (4) it is necessary to have an equation of state for the gas mixture, i. e., volumetric data for the mixture as a function of pressure and composition at the temperature of interest.

3. Previously Proposed Methods for Predicting Solubility of Solids in Compressed Gases

During the past dozen years there has been a variety of publications dealing with the calculation of φ_2 as given by (4). In each case a particular equation of state is used and a particular set of mixing rules is employed to predict the volumetric properties of the gas mixture using only experimental data on the pure components. Equations of state which have been used for this purpose include those proposed by Benedict, Webb, and Rubin; by Beattie and Bridgeman; by Redlich and Kwong, and by Martin and Hou [4, 5]. In a similar but slightly different approach, attempts have been made to calculate φ_2 using a pseudocritical method and generalized thermodynamic charts as described by Joffe [6]. In some cases these methods have produced good results; in others the results have been only fair, and in a few cases the results have been poor. The absence of consistently good results is due to the inadequacy

of the equations of state and, more important, to the very rough nature of the empirical mixing rules which are used to relate mixture constants to those of the pure components. In some cases such rules are reliable but in others they are not, and it is very difficult in the absence of pertinent experimental information to decide a priori whether or not a given mixing rule is likely to be appropriate for a given mixture.

The most reliable method for calculating φ_2 uses the theoretically valid equation of state known as the virial equation. Although this equation was originally proposed about sixty years ago on purely empirical grounds, it has been shown to have a sound statistical mechanical basis. The compressibility factor for the gas mixture is given by

$$z = 1 + \frac{B_{\text{mix}}}{v} + \frac{C_{\text{mix}}}{2v^2} + \dots, \quad (6)$$

where v is the molar volume, i.e., $V/(n_1 + n_2)$, and the virial coefficients for the mixture are given rigorously as a function of composition by

$$B_{\text{mix}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (7)$$

$$C_{\text{mix}} = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} . \quad (8)$$

The fugacity coefficient is determined by substituting (6), (7), and (8) into (4), yielding

$$\ln \varphi_2 = \frac{2}{v} (y_1 B_{12} + y_2 B_{22}) + \frac{3}{2v} (y_1^2 C_{112} + 2y_1 y_2 C_{122} + y_2^2 C_{222})$$

$$+ \dots - \ln z. \quad (9)$$

The various virial coefficients B_{ij} and C_{ijk} are functions only of temperature. Various techniques have been proposed for calculating the necessary virial coefficients [7,8]. In general it is possible to make good estimates of the second virial coefficients B_{ij} but, at present, it is not possible to estimate accurately the third virial coefficients C_{ijk} . As a result, use of the virial equation for calculating φ_2 is limited to moderate densities or pressures (typically up to 20-60 atm depending on the temperature and on the nature of the components), and it is not at all useful for equilibria at very high pressure.

4. Calculation of Fugacity Coefficients Using

Redlich's Latest Equation

During the past few years Dr. Otto Redlich and co-workers have developed an equation of state which is an empirical modification of the equation proposed by Redlich and Kwong [9]. The modification is based on the generalized compressibility factor tables of Pitzer et al. [2]. Redlich's equation is of the form

$$z = z_{RK} + f(T_R, P_R, \omega) , \quad (10)$$

where z_{RK} is the compressibility factor as given by the Redlich-Kwong equation and $f(T_R, P_R, \omega)$ is a generalized analytical deviation function whose independent variables are reduced temperature T_R , reduced pressure P_R , and acentric factor ω . The Redlich-Kwong equation is

$$z_{RK} = \frac{v}{v - b} - \frac{a}{RT^{3/2}(v + b)} . \quad (11)$$

The two constants a and b are related to the critical temperature and pressure by

$$a = 0.4278 R^2 \frac{T_c^{2.5}}{P_c} , \quad (12)$$

and

$$b = 0.0867 \frac{RT_c}{P_c} . \quad (13)$$

For a binary mixture of components 1 and 2,

$$a_{mix} = y_1^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2 , \quad (14)$$

and

$$b_{mix} = y_1 b_1 + y_2 b_2 . \quad (15)$$

The function $f(T_R, P_R, \omega)$ is a very complicated but analytical expression obtained by forcing agreement between (10) and Pitzer's generalized tables. To apply $f(T_R, P_R, \omega)$ to a mixture, a pseudocritical hypothesis is used to calculate the reduced temperature, the reduced pressure, and the acentric factor for the mixture. The simplest procedure for doing

so is to accept Kay's rule [4], but it was found by Redlich, et al that an alternate empirical procedure gives a much more accurate representation of volumetric data for gaseous mixtures. The details of this alternate procedure are described in a forthcoming publication [10]. Redlich and co-workers found that their equation reproduced with high accuracy volumetric data for a variety of nonpolar mixtures at moderate and high pressures. However, there were strong indications that at conditions near the critical of the mixture, the equation is not reliable.

In view of the mathematical complexity of Redlich's equation, it is essential to use an electronic computer for calculating φ_2 and for finding the trial-and-error solution to the equation of equilibrium (Equation 1). Dr. Redlich kindly supplied the author with the necessary computer programs.

Calculations with Redlich's equation were performed for four systems for which high-pressure data (beyond the range of the second virial coefficient) were available; in each system the solubility of the heavy (solid) component in the gas phase was calculated. The four systems are: carbon dioxide-nitrogen, carbon dioxide-air, oxygen-hydrogen, and naphthalene-ethylene. The calculated results are compared with experimental solubilities in tables 1, 2, 3, and 4.

In table 1 we compare calculated and experimental results for the carbon dioxide-nitrogen system. The results are expressed in terms

of enhancement factors E defined by

$$E \equiv \frac{y_2 \text{ (actual)}}{y_2 \text{ (ideal)}} , \quad (16)$$

where by $y_2 \text{ (ideal)}$ we mean the value calculated by assuming $\varphi_2 = 1$

and $f_2^s = P_2^s$. Thus

$$y_2 \text{ (ideal)} = \frac{P_2^s}{P} . \quad (17)$$

Results are shown for the temperature range 140° to 190°K and for pressures up to 100 atm. For all temperatures except the lowest, agreement between calculated and experimental results is very good. At 140°K the agreement is somewhat worse, although still not bad. Deviations between experimental and calculated results at high pressure at this low temperature are probably due to the fact that the mixture is not far removed from its critical state, where Redlich's equation (as all other equations of state) is not very reliable.

Table 2 gives calculated and experimental solubilities for the carbon dioxide-air system up to 200 atm for the temperature range 133° to 163°K . Agreement is not good especially at the lower temperatures. Again, the poor agreement at the higher pressures is probably due to the fact that the mixture is not sufficiently removed from its critical conditions.

Table 1. Solid-vapor equilibria for carbon dioxide-nitrogen.
Comparison of predicted and experimental results.

CO ₂	T _c = 304.19° K	P _c = 72.9 atm	ω = 0.225
N ₂	T _c = 126.2° K	P _c = 33.5 atm	ω = 0.04

$$E = y_2 P / P_2^s$$

<u>Pressure, atm</u>	<u>Calculated</u>	<u>Experimental</u> ^[11]
<u>Enhancement factor at 140° K (P₂^s = 0.00184 atm)</u>		
10	1.36	1.3043
20	1.96	1.9565
30	3.18	3.0978
40	5.44	5.4348
50	10.86	11.685
60	21.80	25.435
70	35.40	42.609
80	54.40	60.435
90	65.10	77.283
<u>Enhancement factor at 150° K (P₂^s = 0.00834 atm)</u>		
10	1.32	1.2723
20	1.80	1.6409
30	2.52	2.2830
40	3.62	3.3769
50	5.70	5.5886
60	9.15	9.1320
70	14.02	14.316
80	20.30	21.118
90	27.00	28.894
100	35.00	36.147

Table 1 (continued)

$E = y_2 P / P_2^s$		
<u>Pressure, atm</u>	<u>Calculated</u>	<u>Experimental</u> ^[11]
<u>Enhancement factor at 160° K ($P_2^s = 0.03114$ atm)</u>		
10	1.26	1.2580
20	1.62	1.5987
30	2.12	2.0732
40	2.84	2.7643
50	3.87	3.8694
60	5.55	5.3503
70	7.69	7.4013
80	10.52	10.013
90	13.68	13.213
100	17.42	17.070
<u>Enhancement factor at 170° K ($P_2^s = 0.0993$ atm)</u>		
10	1.22	1.2185
20	1.509	1.4804
30	1.885	1.8369
40	2.34	2.3041
50	3.02	2.9204
60	3.93	3.7341
70	4.83	4.8288
80	6.65	6.1229
90	8.44	7.7946
100	10.59	9.7482

Table 1 (continued)

$$E = y_2 p / p_2^s$$

<u>Pressure, atm</u>	<u>Calculated</u>	<u>Experimental</u> ^[11]
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Enhancement factor at 180° K ($P_2^s = 0.274$ atm)

10	1.193	1.1861
20	1.430	1.3869
30	1.696	1.6533
40	2.04	2.0000
50	2.54	2.4270
60	3.06	2.9562
70	3.81	3.6022
80	4.61	4.3796
90	5.35	5.2883
100	6.75	6.4234

Enhancement factor at 190° K ($P_2^s = 0.697$ atm)

10	1.160	1.1458
20	1.349	1.3402
30	1.589	1.5641
40	1.849	1.8321
50	2.17	2.1576
60	2.58	2.5626
70	3.02	3.0206
80	3.67	3.5700
90	4.30	4.2415
100	5.16	4.0074

Table 2. Solid-vapor equilibria for carbon dioxide-air.

CO ₂	T _c = 304.19° K	P _c = 72.9 atm	w = 0.225
O ₂	T _c = 154.35° K	P _c = 49.7 atm	w = 0.03
N ₂	T _c = 126.2° K	P _c = 33.5 atm	w = 0.04

y₂

<u>Pressure atm (gauge)</u>	<u>Calc. x 10⁴</u>	<u>Expt. x 10⁴ [12]</u>
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Mole fraction of CO₂ in air at 133° K (P₂^s = 0.000567 atm)

10	0.79	0.77
20	0.689	0.62
30	23.2	0.82
40		
50		liquid air

Mole fraction of CO₂ in air at 143° K (P₂^s = 0.00304 atm)

10	4.31	4.19
20	3.06	2.92
30	3.32	3.54
40	32.1	5.19
50	39.6	7.39
60	45.0	13.1
70	49.4	17.1
80	53.7	18.8
100	59.6	22.9
150	71.5	27.3
200	83.1	30.2

Table 2 (continued)

Pressure atm (gauge)	y_2	
	Calc. $\times 10^4$	Expt. $\times 10^4$ [12]
Mole fraction of CO_2 in air at 152°K ($P_2^s = 0.01129 \text{ atm}$)		
10	13.92	12.8
20	9.97	8.65
30	9.68	8.33
40	11.62	99.33
50	21.20	12.20
60	54.70	15.1
70	71.90	22.2
80	84.10	28.0
90	94.40	34.7
100	97.10	39.0
150	123.2	52.0
200	142.0	58.1
Mole fraction of CO_2 in air at 163°K ($P_2^s = 0.0456 \text{ atm}$)		
10	53.6	49.2
20	36.1	33.6
30	32.2	28.1
40	33.2	28.5
50	38.4	30.6
60	50.1	36.5
70	72.0	43.3
80	98.4	52.9
90	121.0	61.0
100	141.0	69.5
150	203.0	94.9
200	240.0	123.0

Table 3 gives calculated and experimental solubilities for the oxygen-hydrogen system up to 50 atm for the temperature range 40-53°K. At normal temperatures 50 atm is not considered to be a very high pressure, but in this case it is relatively very high since the corresponding molar density is large due to the very low temperature. Since hydrogen is a quantum fluid which does not obey the classical theorem of corresponding states, effective critical properties rather than actual critical constants were used. The effective values were determined by obtaining optimum agreement between calculated and observed volumetric properties of gaseous hydrogen.

The agreement between calculated and experimental solubilities is surprisingly good. The lowest temperature (40°K) is only about 7°K above the (true) critical temperature of hydrogen and one might expect that the calculations would be poor because of proximity to critical conditions. However, at this low temperature level, 7°K is a large amount. Furthermore, at 40°K the mole fraction of oxygen in the gas phase is of the order of 10^{-6} and therefore must have a very small effect on the critical properties of the gaseous mixture.

Finally, table 4 gives results for the solubility of naphthalene in ethylene up to 270 atm for the temperature range 285-323°K. The critical temperature of ethylene is 282°K. The results are only fair; at the higher pressures the calculated and experimental values differ by

Table 3. Solid-vapor equilibria for oxygen-hydrogen.
Comparison of predicted and experimental results.

O_2	$T_c = 154.35^\circ K$	$P_c = 49.7 \text{ atm}$	$\omega = 0.03$
H_2 (pseudo)	$T_c = 40^\circ K$	$P_c = 28 \text{ atm}$	$\omega = 0$

<u>Pressure, atm</u>	<u>y_2</u>	
	<u>Calculated</u>	<u>Expt.</u> [13, 14]
<u>Mole fraction of O_2 in H_2 at $40^\circ K$ ($P_2^s = 1.585 \times 10^{-6} \text{ atm}$)</u>		
5	5.72×10^{-7}	1.2×10^{-6}
10	5.53×10^{-7}	1.4×10^{-6}
15	7.94×10^{-7}	1.1×10^{-6}
20	1.56×10^{-6}	3.0×10^{-6}
30	2.82×10^{-5}	
40	2.82×10^{-3}	
50	4.28×10^{-3}	
<u>Mole fraction of O_2 in H_2 at $48^\circ K$ ($P_2^s = 1.286 \times 10^{-4} \text{ atm}$)</u>		
5	3.78×10^{-5}	3.73×10^{-5}
10	2.84×10^{-5}	2.81×10^{-5}
15	2.9×10^{-5}	2.8×10^{-5}
20	3.43×10^{-5}	3.7×10^{-5}
30	6.14×10^{-5}	7.0×10^{-5}
40	1.4×10^{-4}	1.65×10^{-4}
50	3.78×10^{-4}	2.70×10^{-4}

Table 3 (continued)

<u>Pressure, atm</u>	<u>y₂</u>	
	<u>Calculated</u>	<u>Expt.</u> [13, 14]
Mole fraction of O ₂ in H ₂ at 53° K (P ₂ ^s = 8.95 x 10 ⁻⁴ atm)		
5	2.38 x 10 ⁻⁴	2.2 x 10 ⁻⁴
10	1.61 x 10 ⁻⁴	1.62 x 10 ⁻⁴
15	1.46 x 10 ⁻⁴	1.3 x 10 ⁻⁴
20	1.515 x 10 ⁻⁴	1.66 x 10 ⁻⁴
30	1.99 x 10 ⁻⁴	2.17 x 10 ⁻⁴
40	3.11 x 10 ⁻⁴	3.15 x 10 ⁻⁴
50	5.31 x 10 ⁻⁴	4.6 x 10 ⁻⁴

as much as a factor of two. This system provides a particularly sensitive test of the calculational method; not only is the system rather near its critical conditions (notice the relatively large mole fraction of naphthalene in the vapor at the higher temperature and pressure), but, in addition, this system is a highly asymmetric one where the solute molecule is a very large one, much larger than the solvent molecule, and already on the borderline of the corresponding states correlation.

Table 4. Solid-vapor equilibrium for naphthalene-ethylene.
Comparison of predicted and experimental results.

$C_{10}H_8$	$T_c = 751.69^\circ K$	$P_c = 40.6 \text{ atm}$	$w = 0.306$
C_2H_4	$T_c = 283.09^\circ K$	$P_c = 50.5 \text{ atm}$	$w = 0.085$

Pressure, atm	y_2	
	Calc. $\times 10^4$	Expt. $\times 10^4$ [15]
Mole fraction of $C_{10}H_8$ in C_2H_4 at $285^\circ K$ ($P_2^s = 3.1 \times 10^{-5} \text{ atm}$)		
140.2	185	106
169.6	226	119
189.8	250	133
237.4	310.5	157
Mole fraction at $298^\circ K$ ($P_2^s = 1.15 \times 10^{-4} \text{ atm}$)		
111.4	72.9	115
126.3	88.8	141
150.6	115	172
189.8	152.2	209
255.9	208	253
Mole fraction at $308^\circ K$ ($P_2^s = 2.92 \times 10^{-4} \text{ atm}$)		
126.3	96.2	170
142.2	121.0	204
145.7	127.9	217
189.8	181.0	301
237.4	234.0	366
270.3	268.0	401

Table 4 (continued)

<u>Pressure, atm</u>	<u>y_2</u>	
	<u>Calc. $\times 10^4$</u>	<u>Expt. $\times 10^4$ [15]</u>
Mole fraction at 318° K ($P_2^s = 7.05 \times 10^{-4}$ atm)		
40.6	1.33	4.8
45.4	1.59	3.4
52.0	2.13	7.0
61.2	3.52	8.3
70.4	6.51	9.8
79.8	13.2	23.9
98.5	41.4	85.4
117.4	78.2	175.5
121.2	87.9	191.5
137.2	125	257
142.2	139	286
156.4	168	351
185.1	220	471
208.8	262	575
237.4	306	676
270.3	356	766
Mole fraction at 323° K ($P_2^s = 1.070 \times 10^{-3}$ atm)		
46.6	2.27	13.9
65.2	5.37	15.6
75.1	9.84	18.8
84.7	18.31	33.9
94.2	32.3	61.4
103.9	49.5	98.0
113.6	70.2	157.5
123.0	91.6	220
132.4	116.0	294
142.2	134.0	378
151.8	161.0	461
161.0	185.5	563

Table 4 (continued)

<u>Pressure, atm</u>	<u>y₂</u>	
	<u>Calc. x 10⁴</u>	<u>Expt. x 10⁴ [15]</u>
<u>Mole fraction at 323° K (P₂^s = 1.070 x 10⁻³ atm) (cont'd)</u>		
175.5	218	739
189.8	246	1075
204.2	256	1534
218.3	273	1654
237.4	298	1737
270.3	362	1798

In summary, it appears that Redlich's equation of state is capable of giving fairly good predictions of the solubility of a solid in a compressed gas. Predicted values are probably good at least within a factor of 2, and at conditions remote from critical they are undoubtedly much better than that. Like all equations of state, Redlich's is least reliable in the critical region. The great advantage of doing solubility calculations based on Redlich's equation is that the calculations may easily be performed with an electronic computer and require no more than the critical temperature, critical pressure and acentric factor of each component.

5. Calculations Based on Regular Solution Theory

A dense gas is usually considered as an extreme case of a very nonideal gas, and by using the ideal gas as a reference state, fugacity coefficients can be calculated from volumetric properties; this approach is the common one of dealing with dense gas mixtures, and this was the one used in the previous section. An alternate approach, however, is suggested by the fact that a dense gas may be considered as an expanded liquid. When this view is adopted the thermodynamic properties of the mixture are calculated not from volumetric properties but from a suitable theory of liquid solutions. For nonpolar components a simple and reasonable description of liquid mixtures is given by the Hildebrand-Scatchard theory of regular solutions.

6. Fundamental Thermodynamic Equations

We consider the equilibrium between a solid designated by subscript 2 and a dense fluid (subscript 1) and we wish to find the solubility x_2 in the fluid phase. The thermodynamic relations appropriate for this situation are well known and are briefly summarized below.

The overall equation of equilibrium in terms of fugacities is

$$f_2^s = f_2^f, \quad (18)$$

where the superscripts s and f designate the solid and fluid phases. For

convenience we rewrite the equation of equilibrium:

$$RT \ln \frac{f_2^L(\text{pure})}{f_2^s} + RT \ln \frac{f_2^f}{f_2^L(\text{pure})} = 0 \quad , \quad (19)$$

where $f_2^L(\text{pure})$ is the fugacity of pure subcooled liquid 2 at T , the temperature of interest. The first term in (19) is the Gibbs energy change of going, at temperature T and pressure P , from pure solid 2 to pure subcooled liquid 2. The second term in (19) is the partial Gibbs energy change experienced by subcooled liquid 2 as it goes, at temperature T , from the pure state to the solution in the fluid where its mole fraction is x_2 . The first term in (19) is given in terms of pure-component properties of component 2:

$$RT \ln \frac{f_2^L(\text{pure})}{f_2^s} = \Delta h_{\text{fusion at } T_m} \left[1 - \frac{T}{T_m} \right] - \int_T^{T_m} \Delta c_p dT + T \int_T^{T_m} \frac{\Delta c_p}{T} dT \\ + \int_{P_2}^P \Delta v dP \quad , \quad (20)$$

where $\Delta h_{\text{fusion at } T_m}$ is the molar enthalpy of fusion at the normal melting temperature T_m and,

$$\Delta c_p \equiv c_p^{\text{liquid}} - c_p^{\text{solid}} \quad (21)$$

$$\Delta v \equiv v^{\text{liquid}} - v^{\text{solid}} , \quad (22)$$

where c_p is the molar specific heat at (low) constant pressure, v is the molar volume at temperature T , and P_2^s is the saturation (vapor) pressure of the solid at T .

The second term in (19) is given by

$$RT \ln \frac{f_2^f}{f_2^L(\text{pure})} = RT \ln \gamma_2 + RT \ln x_2 , \quad (23)$$

where the activity coefficient γ_2 refers to pure subcooled liquid 2 at temperature T and pressure P as the standard state. This activity coefficient is given by the regular solution theory [2]:

$$RT \ln \gamma_2 = v_2^L \Phi_1^2 (\delta_1 - \delta_2)^2 , \quad (24)$$

where v_2^L is the molar volume and δ_2 the solubility parameter of pure subcooled liquid 2, and δ_1 is the solubility parameter of the (fluid) solvent, all at temperature T and pressure P . Under the conditions of interest here, $x_2 \ll 1$ and therefore Φ_1 , the volume fraction of solvent, is for all practical purposes equal to unity. When (20), (23), and (24) are substituted into (19) we obtain, for the desired solubility x_2 ,

$$RT \ln \frac{1}{x_2} = \Delta h_{\text{fusion at } T_m} \left[1 - \frac{T}{T_m} \right] - \int_T^{T_m} \Delta c_p dT + T \int_T^{T_m} \frac{\Delta c_p}{T} dT \\ + \int_{P_2}^P \Delta v dP + v_2^L \Phi_1^2 (\delta_1 - \delta_2)^2 . \quad (25)$$

In (25) the important terms on the right-hand side are the first and the last. The terms involving Δc_p and Δv are of secondary importance.

7. Evaluation of Parameters

The heat of fusion, the normal melting point, and the molar volume of a typical nonpolar solid are usually available from the literature. The specific heats of the pure liquid and solid are also known, at least for the more common substances; frequently, however, they are not known as a function of temperature in which case Δc_p may be treated as a constant with little error. Figures 1 and 2 give the f^S/f^L ratios for subcooled liquid carbon dioxide and for subcooled liquid naphthalene.

The molar volume of the subcooled liquid must be obtained by extrapolation; since the density of a liquid at temperatures near the melting point does not vary appreciably, this extrapolation is not a sensitive factor in applying (25). Molar volumes of subcooled liquid carbon dioxide and subcooled liquid naphthalene are shown in figures 3 and 4.

Much more important is the evaluation of the two solubility

parameters δ_1 and δ_2 . The solubility parameter is defined by

$$\delta_1 \equiv \left(\frac{\Delta u_i}{v_i} \right)^{1/2}, \quad (26)$$

where v_i is the molar volume of component i at the temperature T and pressure P where its solubility parameter is desired, and where

$$\Delta u_i = u_i(T, \infty) - u_i(T, v_i), \quad (27)$$

$u_i(T, \infty)$ is the internal energy of i at temperature T and at infinite volume (i.e., ideal gas) and $u_i(T, v_i)$ is the internal energy of i at temperature T and molar volume v_i .

First we consider the heavy component 2. Assuming that sub-cooled liquid 2 is incompressible and that its saturation (vapor) pressure is small (say, less than a few atmospheres),

$$\delta_2 = \left(\frac{\Delta h_{\text{vap at } T} - RT}{v_2} \right)^{1/2} \quad (28)$$

The enthalpy of vaporization Δh_{vap} must be evaluated at temperature T ; since T is below the melting temperature T_m this enthalpy of vaporization must be found by extrapolation using the equation

$$\Delta h_{\text{vap at } T} = \Delta h_{\text{vap at } T'} + \int_{T'}^T (c_p^L - c_p^V) dT , \quad (29)$$

where c_p^L and c_p^V are the molar specific heats of the saturated liquid and vapor, respectively. The (arbitrary) temperature T' is some convenient temperature in the real liquid region where the heat of vaporization is known accurately. Table 5 gives solubility parameters for subcooled liquid carbon dioxide.

The solubility parameter δ_1 is for the fluid solvent, i.e., the dense gas. Since the volume of the gas is highly dependent on the pressure it follows that δ_1 (unlike δ_2) is a strong function of pressure. The volume of the gas is given by

$$v_1 = z \frac{RT}{P} , \quad (30)$$

and the compressibility factor z is given by Pitzer and Brewer [2] in the form

$$z = z^{(0)}(P_R, T_R) + \omega z^{(1)}(P_R, T_R) , \quad (31)$$

where $z^{(0)}$ and $z^{(1)}$ are generalized, tabulated functions of reduced pressure P_R and reduced temperature T_R and ω is the acentric factor defined by

Table 5. Solubility parameters for subcooled liquid carbon dioxide from pure-component data.

<u>Temperature, °K</u>	<u>δ, (cal/cc)^{1/2}</u>
140	11.71
150	11.42
160	11.19
170	10.89
180	10.58

$$\omega \equiv -\log_{10} \left(\frac{P^s}{P_c} \right)_{T_R = 0.70} - 1.000, \quad (32)$$

where P_c is the critical pressure and P^s is the saturation (vapor) pressure at $T_R = 0.70$.

The change in internal energy given by (27) can also be found from Pitzer's generalized tables for the isothermal effect of pressure on enthalpy by using the relation between internal energy and enthalpy:

$$\Delta u = \Delta h - \Delta(Pv), \quad (33)$$

where

$$\Delta h = h(T, P = 0) - h(T, P). \quad (34)$$

For $\Delta(Pv)$ we write

$$\Delta(Pv) = RT \Delta z \quad (35)$$

with

$$\Delta z = z(\text{ideal gas}) - z(P, T) . \quad (36)$$

Figures 5 and 6 show reduced solubility parameters as a function of reduced temperature and reduced pressure for two values of acentric factor. Figure 7 gives the solubility parameter of liquid and gaseous nitrogen over a wide range of pressure and temperature including the critical region where the solubility parameter is very sensitive to small changes in temperature or pressure. Data for the preparation of figure 7 were taken from Strobridge [16].

8. The Carbon Dioxide-Nitrogen System

Equation (25) was used to calculate the solubility of solid carbon dioxide in nitrogen in the region 140-170°K and 90-200 atm. When the calculated results are compared with experimental solubilities [11] the comparison shows that the calculated results are too low by one order of magnitude. This poor result is undoubtedly due to the fact that the solubility x_2 is very sensitive to the values of δ_1 and δ_2 ; even a slight change in $\delta_1 - \delta_2$ can seriously affect the solubility. This sensitivity is necessarily always present whenever δ_1 and δ_2 are very different from one another, as they are in this case and as one may expect them to be in any solid-dense gas equilibrium situation. It therefore appears likely that the regular solution approach described above is not useful for

accurately predicting solubilities from pure-component data alone. However, (25) is a very useful equation for correlation and extrapolation of solubility data provided at least some data for the binary system are available.

9. Correlation of Solubility Data

Equation (25) may be considered as a semi-empirical correlating equation if δ_2 , the solubility parameter of the solute, is treated as an empirical parameter, dependent on temperature but not on pressure. For example, table 6 gives the solubility parameter of naphthalene as calculated from the regular solution equation and from solubility data in saturated liquid carbon dioxide [17]; figure 8 gives the solubility parameters of carbon dioxide which were used. The solubility parameter of naphthalene calculated in this way is close to, but not identical with, the solubility parameter calculated from pure-component properties as given by (28) and (29). Figure 9 shows the solubility parameter of naphthalene as calculated from solubility data in compressed ethylene at several temperatures and pressures. These solubility parameters are somewhat lower than those determined from solubility data in carbon dioxide. Figure 9 shows that δ_2 is essentially invariant with pressure which is consistent with the derivation of (25). The pressure-sensitive term in (25) is δ_1 , the solubility parameter of the gaseous solvent, as indicated by figures 5 and 6.

Table 6. Solubility parameters for subcooled liquid naphthalene from solubility measurements in liquid carbon dioxide.

<u>Temperature, °C</u>	<u>δ, (cal/cc)^{1/2}</u>
-20	12.20
-10	11.85
0	11.46
10	10.97
20	10.33
25	9.90

Equation (25) with figures 5 and 6 correctly predicts that the solubility of a solid in a dense fluid changes very rapidly with temperature and pressure in the vicinity of the critical temperature and pressure of the solvent; near the critical point, δ_1 is very sensitive to small changes in temperature and pressure as shown by figures 5, 6, and 7. Equation (25) indicates that near the critical point of the solvent a small increase in pressure or a small decrease in temperature can increase the solubility of a solid by one or more orders of magnitude. Such effects have been observed in the nitrogen-hydrogen system [13] and in the carbon dioxide-air system [18].

Application of (25) for the correlation of solid-dense gas solubility data was mentioned by Omar and Dokoupil [19] in their study of

the solid nitrogen-liquid hydrogen system.

10. Conclusion

This study shows once again the validity of a remark made by Professor Pitzer some years ago when he said that while our understanding of the liquid state is small, our understanding of the dense-gas state is still smaller. In both the liquid state and in the dense-gas state we are held back by our lack of knowledge concerning intermolecular forces in multi-body assemblies. However, in the liquid state the geometry of the assembly is at least reasonably regular and the density of a liquid (well below the critical point) is only a mild function of temperature and a very weak function of pressure. As a result it is not surprising that various lattice-type theories of liquids and liquid mixtures are reasonably successful, at least for approximation purposes; the simplification that a liquid is a "loose" solid is a fairly good one for describing thermodynamic properties of liquid solutions. However, in a dense gas, this simplification is no longer applicable; the density is a very strong function of temperature, pressure, and composition--especially at conditions not far removed from the critical.

This study has briefly considered two approaches to the problem of solid-dense fluid equilibria. The first approach considers the dense fluid as a highly nonideal gas and starting out from the ideal-gas limit, attempts to correct for the nonideality by pure-component empirical

constants, generalized by the theorem of corresponding states. This approach is only moderately successful primarily because the extension to mixtures of corresponding states correlations for pure components is based on fixed but essentially arbitrary mixing rules. Unfortunately, these rules are not invariant with the system under consideration nor with the conditions of temperature, pressure, and composition.

The second approach considers the dense fluid as a liquid mixture and the solid solute as a hypothetical pure liquid whose properties are estimated by extrapolation. This extrapolation necessarily becomes increasingly uncertain as the temperature under consideration departs more and more from the melting temperature of the solid. The process of dissolving the hypothetical liquid in the "liquid" solvent is treated as a constant volume process, and again, somewhat arbitrarily, the intermolecular forces between solute and solvent are calculated in a fixed manner from those of the pure components by a geometric-mean assumption. These various simplifications, especially the last one, place a heavy strain on the difference between theory and reality. What clearly is needed is a better theory of fluids in the vicinity of the critical point; such theory is now under active development by workers in statistical mechanics and will, in time, be useful for increasing our ability to describe solid-dense gas equilibria.

11. Acknowledgment

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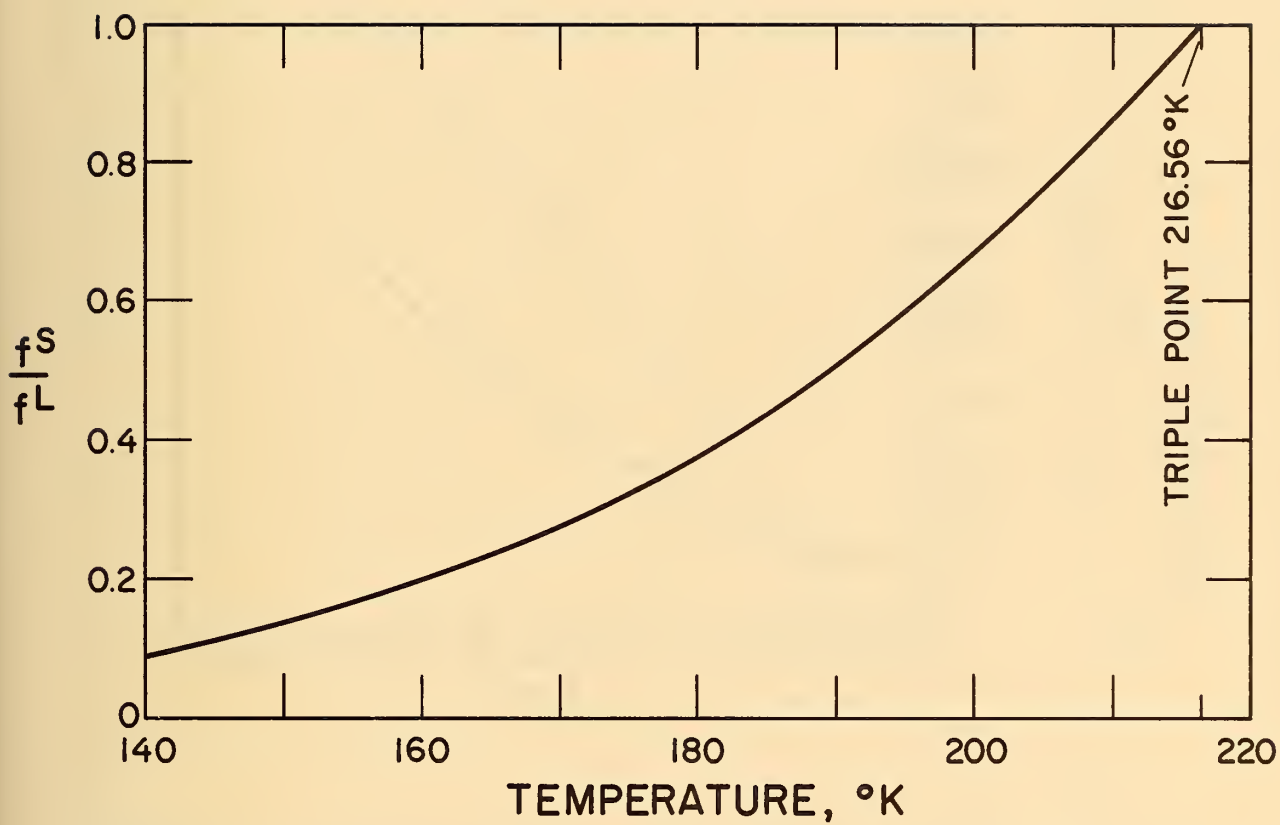


Fig. 1. Fugacity ratio for solid and (subcooled) liquid carbon dioxide.

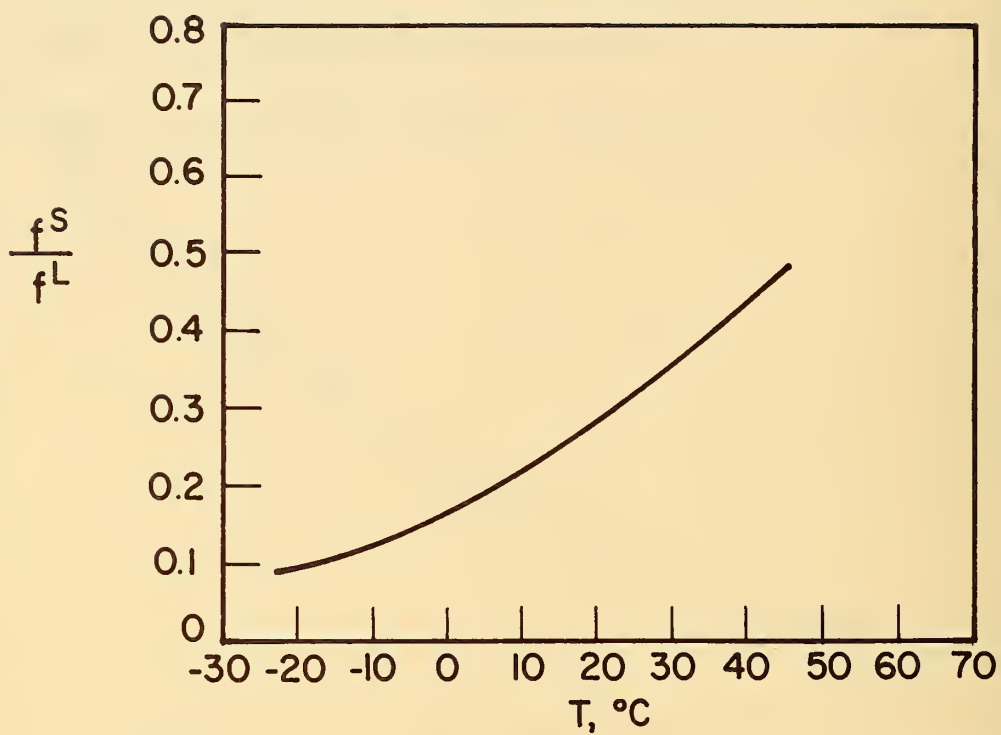


Fig. 2. Fugacity ratio for solid and (subcooled) liquid naphthalene.

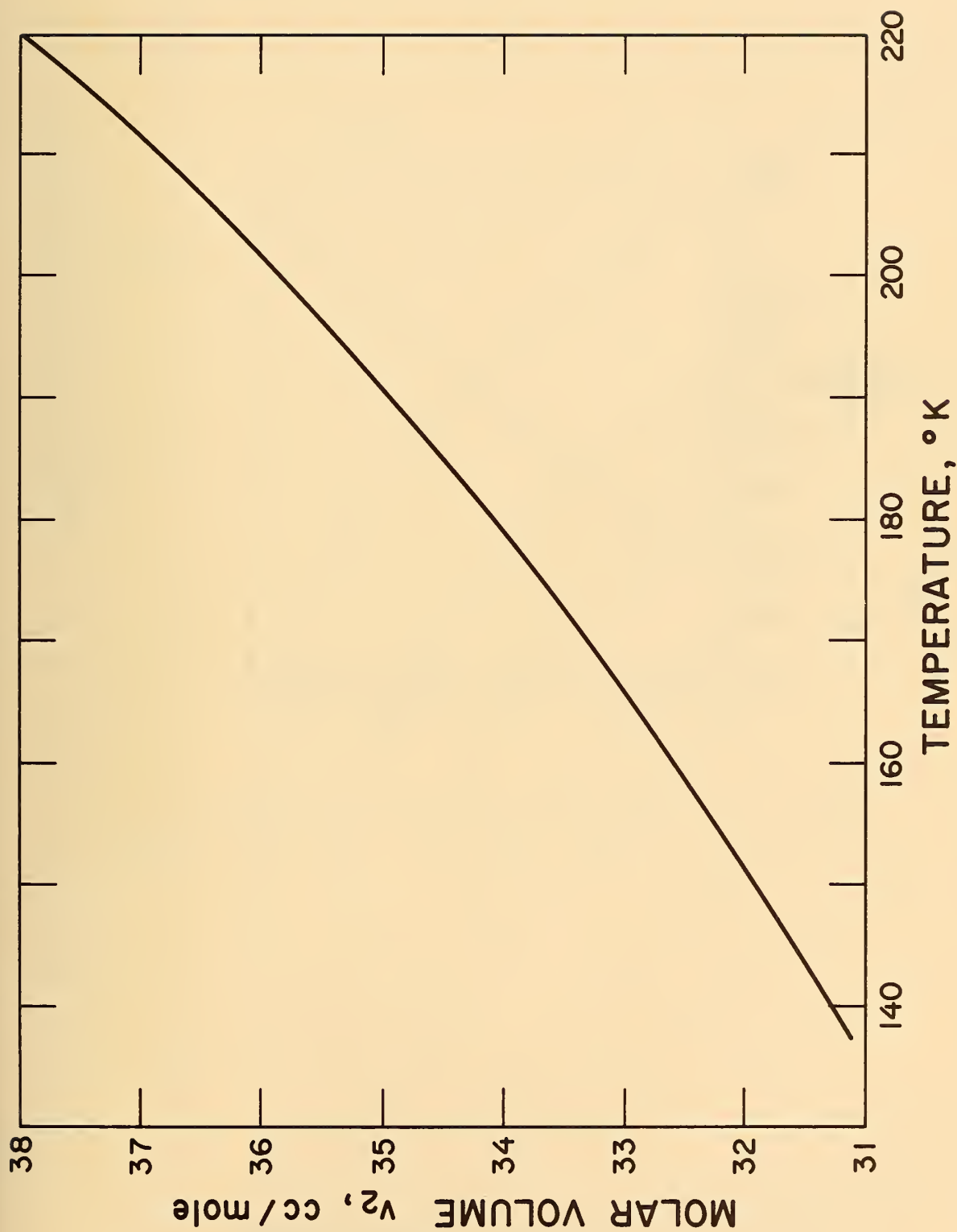


Fig. 3. Molar volume of (subcooled) liquid carbon dioxide.

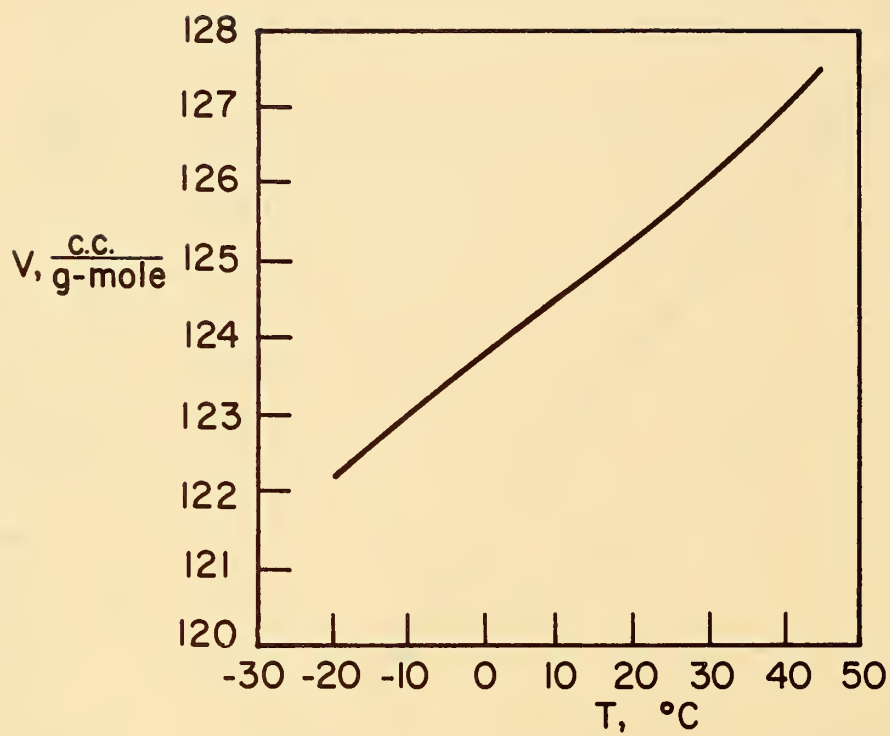


Fig. 4. Molar volume of (subcooled) liquid naphthalene.

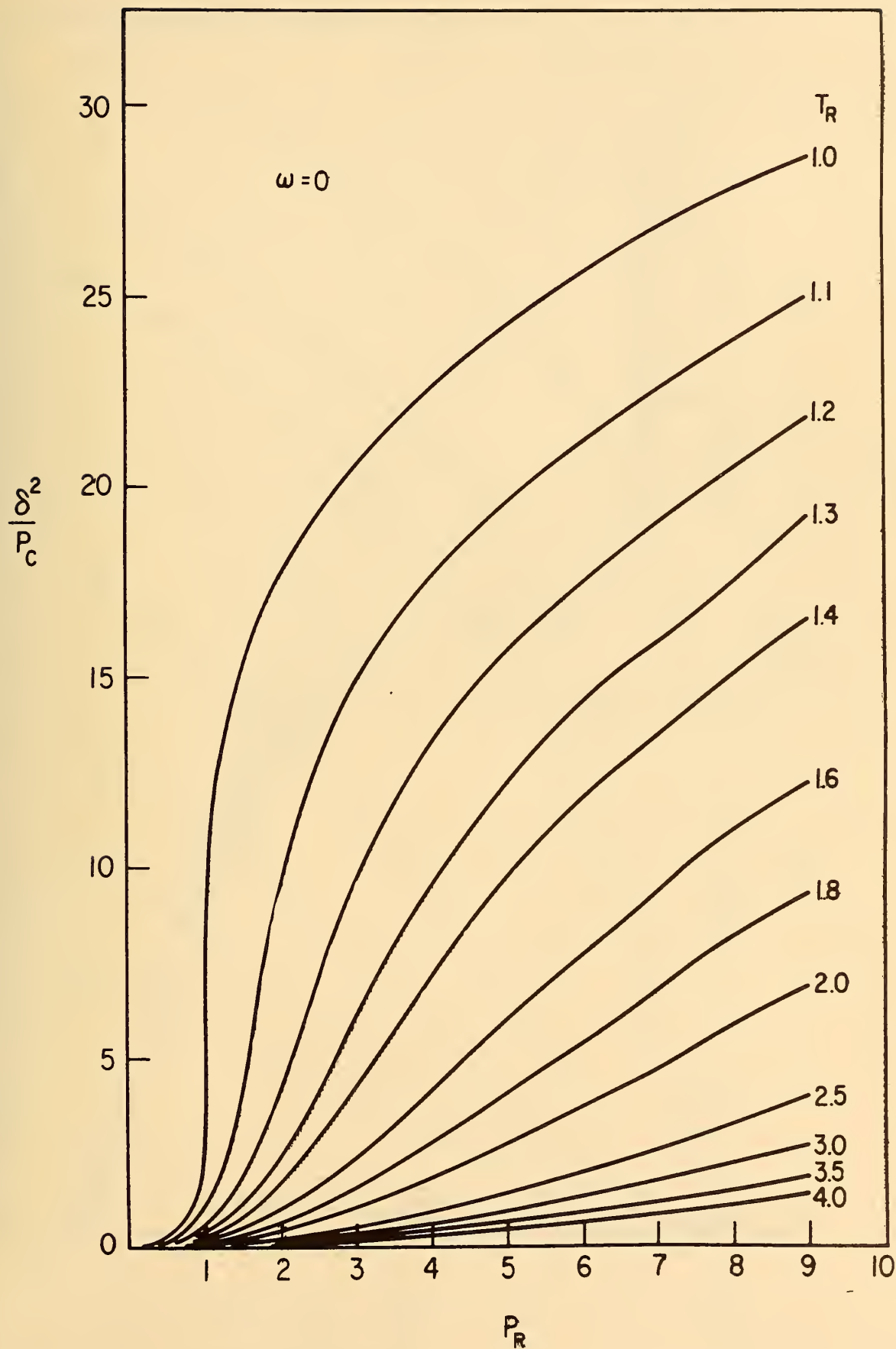


Fig. 5. Solubility parameters for dense gases with an acentric factor of zero.

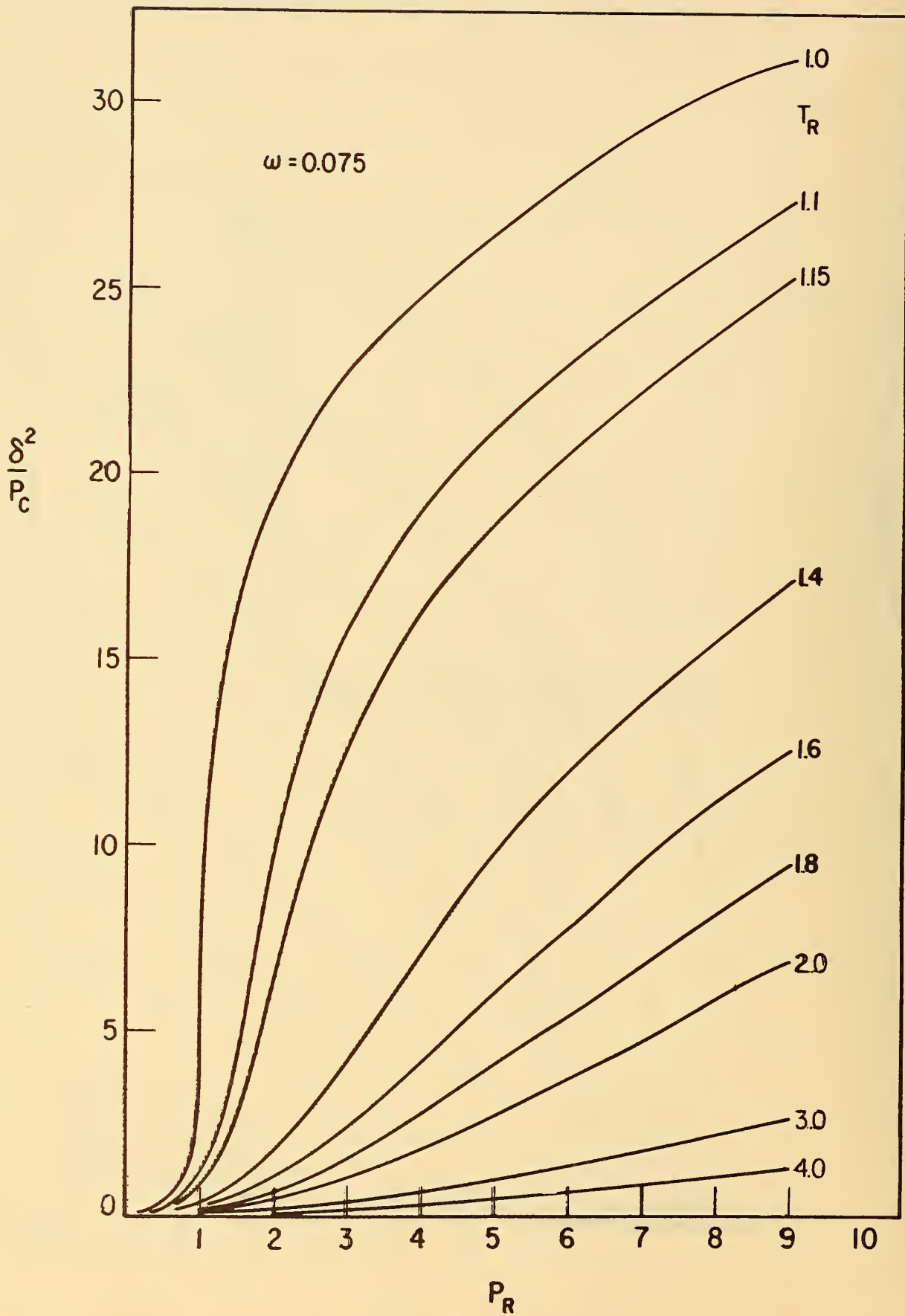


Fig. 6. Solubility parameters for dense gases with an acentric factor of 0.075.

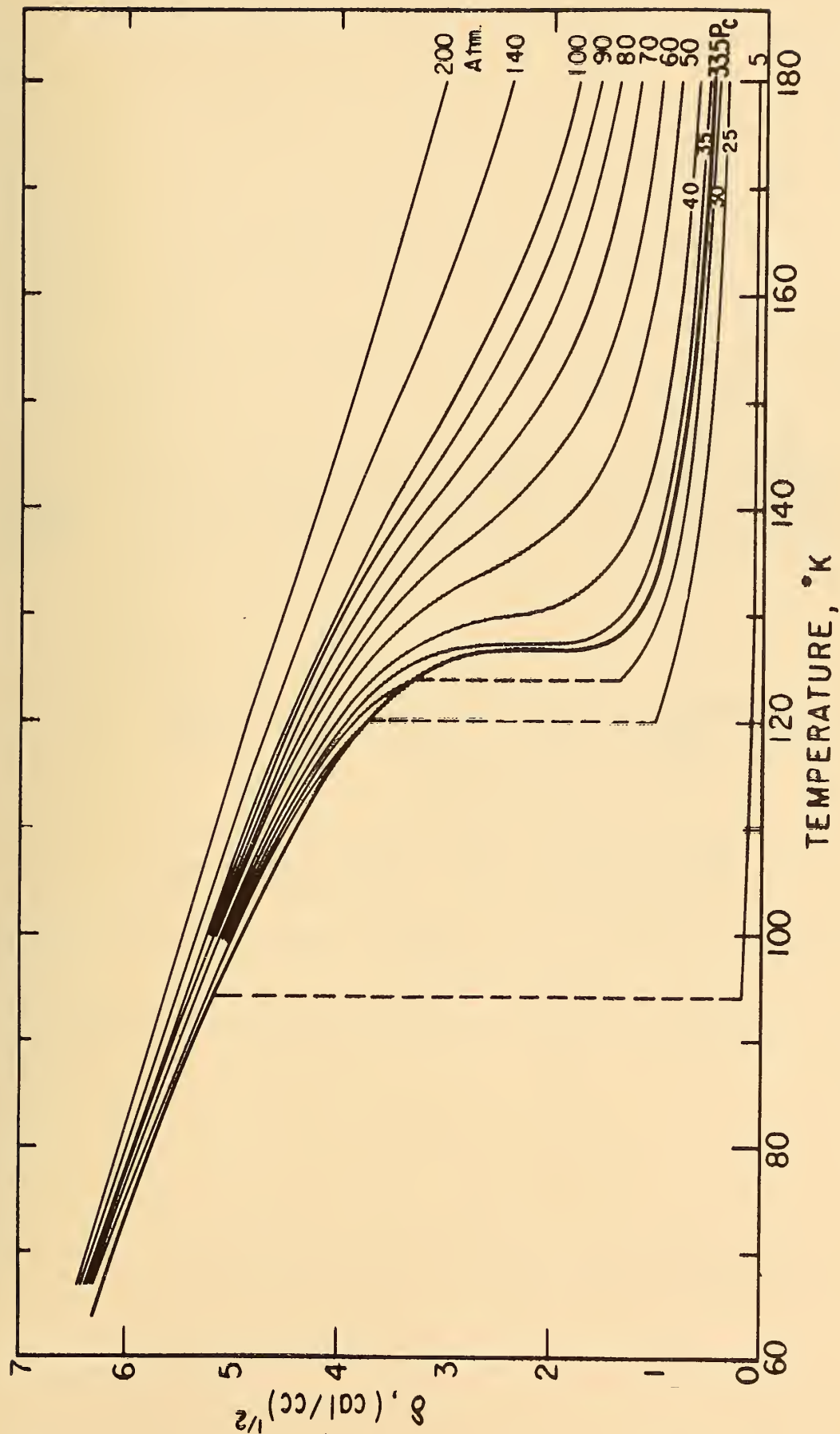


Fig. 7. Solubility parameter for nitrogen.

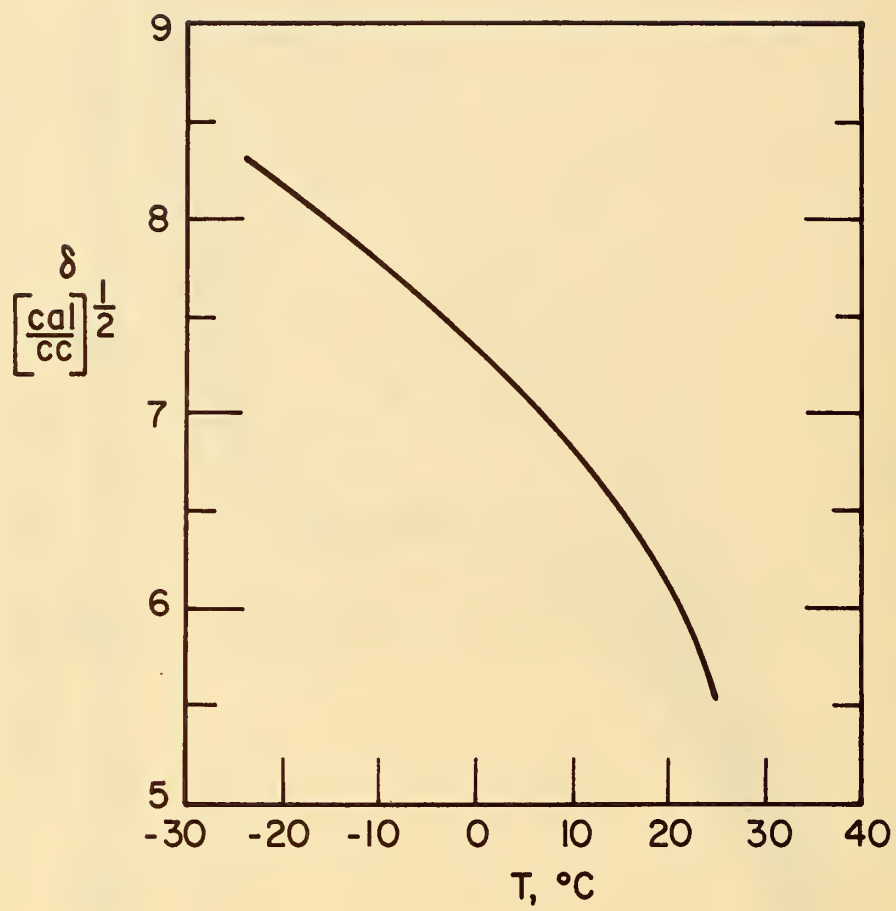


Fig. 8. Solubility parameter for saturated liquid carbon dioxide.

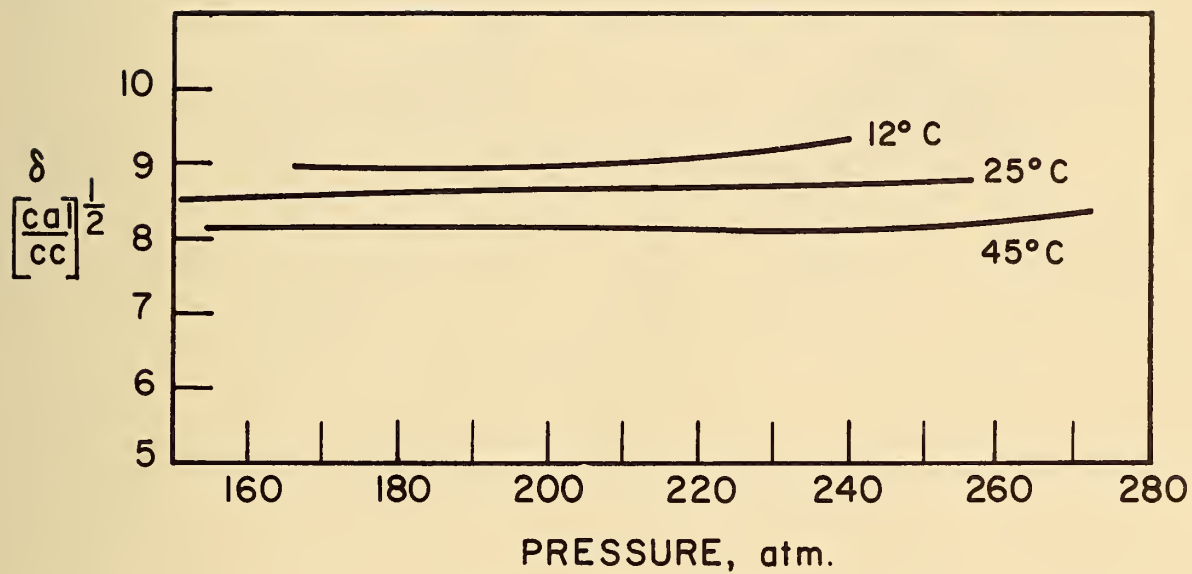


Fig. 9. Solubility parameter of naphthalene calculated from solubility data in gaseous ethylene.

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